Oxoalkyls of Rhenium-(V) and-(VI). *X*-Ray Crystal Structures of $(Me_4ReO)_2Mg(thf)_4$, $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$, $Re_2O_3Me_6$, and $Re_2O_3(CH_2SiMe_3)_6$†

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The interaction of Grignard reagents with Re_2O_7, $[Me_3NH][ReO_4]$, $ReOCl_4$, or $ReOCl_3(PPh_3)_2$ leads to the diamagnetic rhenium(V) complexes $(Me_4ReO)_2Mg(thf)_4$ and $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$ (thf = tetrahydrofuran) whose structures have been determined by *X*-ray crystallography and shown to consist of Mg^{2+} co-ordinated by thf and R_4ReO^- (R = Me or CH_2SiMe_3). Both rhenium(V) species can be oxidised to the previously known rhenium(VI) compounds $ReOR_4$ and $Re_2O_3(CH_2SiMe_3)_6$. A novel high-yield synthesis of $Re_2O_3(CH_2SiMe_3)_6$ and the preparation of the previously unknown $Re_2O_3Me_6$ are reported. The *X*-ray crystal structures of these compounds have been determined to reveal linear Re–O–Re bridges with mutually *trans*-Re=O groups. An *o*-xylenediyl complex $\{[o-(CH_2)_2C_6H_4]_2ReO\}_2Mg(thf)_4$ has also been characterised.

In previous papers we have described the synthesis and properties of various oxoalkyls of rhenium(VI), $ReOR_4$ (R = Me[1,2] or CH_2SiMe_3[1]) and $Re_2O_3(CH_2SiMe_3)_6$,[1] and rhenium(VII), *cis*-ReO_2Me_3;[2] e.s.r.[3] and photoelectron (p.e.) spectra[4] of $ReOR_4$ were also described. An improved synthesis of $ReOMe_4$ and the synthesis and structures of some rhenium oxo-alkoxides were also reported.[5]

Although heterogeneous alkene-metathesis catalysts have been prepared by interaction of, for example, $SnPh_4$ with Re_2O_7 on oxide supports,[6] we are not aware of the synthesis of characterisable alkyl compounds from oxides or oxo-anions other than that of $OsO(CH_2SiMe_3)_4$[7] obtained by interaction of OsO_4 with $Mg(CH_2SiMe_3)_2$.

We report here, *inter alia*, studies on the direct alkylation of dirhenium heptaoxide, $Me_3SiOReO_3$, and trimethylammonium per-rhenate. Analytical data for the various compounds described are collected in Table 1 and spectroscopic data in Table 2.

Results and Discussion

Synthesis and Structure of $(Me_4ReO)_2Mg(thf)_4$.—The interaction of trimethylammonium per-rhenate with seven equivalents of MgMeCl or $MgMe_2$ in tetrahydrofuran (thf) leads to good yields of the orange-red crystalline complex of the above stoicheiometry. The complex may also be obtained using the oxide, Re_2O_7, or by the interaction of either $ReOCl_4$ or $ReOCl_3(PPh_3)_2$ with five equivalents of MgMeCl.

The compound is very rapidly oxidised by oxygen giving initially $ReOMe_4$; the latter can best be obtained by careful addition of hydrogen peroxide to a solution of the compound in thf. It seems certain that the formation of $ReOR_4$ by the previously described procedures,[1,2,5] where the presence of oxidising agent was found to be necessary, involved $[ReOR_4]^-$ species. Although polarographic studies on $ReO(CH_2SiMe_3)_4$ showed[1] that a one-electron reduction to the anion occurred, no study was made on $ReOMe_4$. The $ReOMe_4$ can be further oxidised by O_2, probably to peroxo-species[3] and eventually to ReO_3Me.[8]

The crystalline complex $(Me_4ReO)_2Mg(thf)_4$, on heating above 130 °C or under vacuum, loses thf and collapses to a red powder. The complex is soluble in ethers and mixtures of thf and aromatic hydrocarbons, but is insoluble in light petroleum. It slowly decomposes in halogenated solvents even in absence of air.

The co-ordinated thf can be replaced by *NNN'N'*-tetramethylethylenediamine or 2,2'-bipyridyl but the crystalline products, plates and rhombs respectively, are much less soluble in toluene than is the thf solvate.

The i.r. spectrum shows bands at 1 035s br, 960s br, 920 (sh), and 890m br cm^{-1} that can be assigned to Re=O and to skeletal vibrations and CH_2 rocking modes of thf[9] shifted on co-ordination to lower frequencies compared to free thf. The band at 1 035 cm^{-1} is probably due to $\nu_{asym.}(COC)$ and that at 960 cm^{-1} to ν(Re=O).[10,11] The broad band at 540 cm^{-1} is assigned to Re–C vibrations[1] and the bands at 370 and 320 cm^{-1} to Mg–O stretches.[12] The ^1H spectrum suggests non-rigid behaviour for the five-co-ordinate Me_4ReO grouping since the methyl resonance at δ 2.98 p.p.m. is broad at 25 °C but a sharp singlet at −40 °C. At −40 °C the $^{13}C-\{^1H\}$ spectrum (apart from thf resonances at 69.07 and 25.05) has a single CH_3 group peak at δ 29.50 which collapses to a quartet [*J*(C–H) = 120.64 Hz] in the 'gated' spectrum.

The diamagnetism and stoicheiometry suggested that $[ReOMe_4]^-$ units were co-ordinated to solvated Mg^{2+} and this formulation is confirmed by an *X*-ray structural study which reveals a centrosymmetric structure for the compound (Figure 1). Some important molecular-geometry parameters are given in Table 3. The Mg atom lies on an inversion centre and is octahedrally co-ordinated to four thf groups and two $O=ReMe_4$ units in *trans* positions. The unique Mg=O bond distances, 2.075(9) and 2.100(8) Å, involving the thf groups and 2.029(8) Å, involving the oxo-oxygen of the $O=ReMe_4$ units, are comparable with the corresponding values in $\{[o-(CH_2)_2C_6H_4]_2WO\}_2Mg(thf)_4$,[10] the closest known analogue to the above

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† Tetrakis(tetrahydrofuran)magnesium bis[tetramethyloxorhenate(V)], bis(tetrahydrofuran)magnesium bis[oxotetrakis(trimethylsilylmethyl)-rhenate(V)], μ-oxo-bis[trimethyloxorhenium(VI)], and μ-oxo-bis[oxo-tris(trimethylsilylmethyl)rhenium(VI)].

Supplementary data available (No. SUP 56297, 9 pp.): thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. Properties and analytical data for rhenium oxoalkyl compounds

			Analysis (%)[a]		
Compound	Colour	M.p. (θ_c/°C)	C	H	O
$(Me_4ReO)_2Mg(thf)_4$	Orange-red	168 (decomp.)[b]	34.0 (34.4)	6.6 (6.7)	11.4 (11.5)
$[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$	Red-purple	210 (decomp.)[b]	37.9 (37.8)	8.1 (8.2)	6.3 (5.0)
$Re_2O_3Me_6$	Orange-red	88—90	14.4 (14.1)	3.6 (3.5)	9.3 (9.4)
$Re_2O_3(CH_2SiMe_3)_6$	Red	148—150	30.5 (30.5)	7.1 (7.0)	4.7 (5.1)
$\{[o-(CH_2)_2C_6H_4]_2ReO\}_2Mg(thf)_4$	Orange-red	>300	50.9 (50.9)	5.6 (5.7)	8.9 (8.5)

[a] Calculated values are given in parentheses. [b] Loses thf at *ca.* 130 °C; decomposition without melting.

Table 2. Hydrogen-1 and $^{13}C-\{^1H\}$ n.m.r. data[a]

Compound	^1H	Assignment	$^{13}C-\{^1H\}$	Assignment
$(Me_4ReO)_2Mg(thf)_4$	2.98 (s, 3)[b]	Re-Me	29.50 (s)[b]	Re-Me
	1.35 (m, 2)	$\beta-CH_2(thf)$	25.05 (s)	$\beta-CH_2(thf)$
	3.39 (m, 2)	$\alpha-CH_2(thf)$	69.07 (s)	$\alpha-CH_2(thf)$
$[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$	0.37 (s, 9)	$Re-CH_2Si\mathit{Me}_3$	4.14 (s)	$Re-CH_2Si\mathit{Me}_3$
	4.40 (s, 2)	$Re-C\mathit{H}_2SiMe_3$	39.75 (s)	$Re-\mathit{C}H_2SiMe_3$
	1.24 (m, 1)	$\beta-CH_2(thf)$	25.22 (s)	$\beta-CH_2(thf)$
	3.44 (m, 1)	$\alpha-CH_2(thf)$	69.59 (s)	$\alpha-CH_2(thf)$
$Re_2O_3Me_6$	2.19 (s, 2)	Re-Me (ax.)[c]	39.92 (s)	Re-Me
	2.31 (s, 1)	Re-Me (eq.)[c]	30.08 (s)	Re-Me
$Re_2O_3(CH_2SiMe_3)_6$	0.18 (s, 9)	$Re-CH_2Si\mathit{Me}_3$ (eq.)[c]	2.02 (s)	$Re-CH_2Si\mathit{Me}_3$
	0.36 (s, 18)	$Re-CH_2Si\mathit{Me}_3$ (ax.)[c]	2.94 (s)	$Re-CH_2Si\mathit{Me}_3$
	3.19 (s, 2)	$Re-C\mathit{H}_2SiMe_3$ (eq.)[c]	39.96 (s)	$Re-\mathit{C}H_2SiMe_3$
	2.59 (d, 2)[d] 3.44 (d, 2)	$Re-C\mathit{H}_2SiMe_3$ (ax.)[c]	49.84 (s)	$Re-\mathit{C}H_2SiMe_3$
$\{[o-(CH_2)_2C_6H_4]_2ReO\}_2Mg(thf)_4$	2.10 (s, 4)	$Re-CH_2$	36.15 (s)	$Re-CH_2$
	6.92 (m, 2)	C_6H_4	125.45 (s)	C_6H_4
	7.03 (m, 2)	C_6H_4	128.79 (s)	C_6H_4
	1.40 (m, 4)	$\beta-CH_2(thf)$	137.28 (s)	C_6H_4
	3.56 (m, 4)	$\alpha-CH_2(thf)$	25.22 (s)	$\beta-CH_2(thf)$
			70.81 (s)	$\alpha-CH_2(thf)$

[a] Referenced to $SiMe_4$ at δ 0.00 p.p.m., in C_6D_6 unless otherwise stated; positive shifts downfield of $SiMe_4$; multiplicities and relative intensities are given in parentheses. [b] In $[^2H_8]$toluene, −40 °C. [c] ax. = axial, eq. = equatorial. [d] J(H–H) = 10.7 Hz.

Table 3. Selected bond lengths (Å) and bond angles (°) for $(Me_4ReO)_2Mg(thf)_4$

O(3)–Re	1.694(8)	O(3)–Mg	2.029(8)
C(1)–Re	2.077(24)	C(1A)–Re	2.109(44)
C(2)–Re	2.108(34)	C(2A)–Re	2.053(56)
C(3)–Re	2.116(29)	C(3A)–Re	2.056(52)
C(4)–Re	2.108(25)	C(4A)–Re	2.101(55)
O(1)–Mg	2.100(8)	O(2)–Mg	2.075(9)
C(1)–Re–O(3)	113.3(8)	C(2)–Re–O(3)	109.8(10)
C(3)–Re–O(3)	115.5(11)	C(4)–Re–O(3)	114.0(12)
C(1A)–Re–O(3)	116.5(20)	C(2A)–Re–O(3)	114.8(19)
C(3A)–Re–O(3)	110.9(14)	C(4A)–Re–O(3)	114.7(15)
O(2)–Mg–O(1)	89.6(4)	O(3)–Mg–O(1)	89.5(4)
O(3)–Mg–O(2)	89.4(4)	Mg–O(3)–Re	175.0(4)

complex, which was obtained by interaction of $WOCl_4$ and the di-Grignard reagent. We have now prepared $(Me_4WO)_2Mg(thf)_4$ and confirmed the structure by *X*-ray crystallography; this work will be described separately. Other tetrahydrofuran-solvated magnesium species such as $(thf)_4Mg(\mu-Cl)_3FeCl_2$[13a] and $[(thf)_3Mg(\mu-Cl)_3Mg(thf)_3]^+$[13b] are known.

The carbon atoms of all the thf groups in $(Me_4ReO)_2Mg(thf)_4$

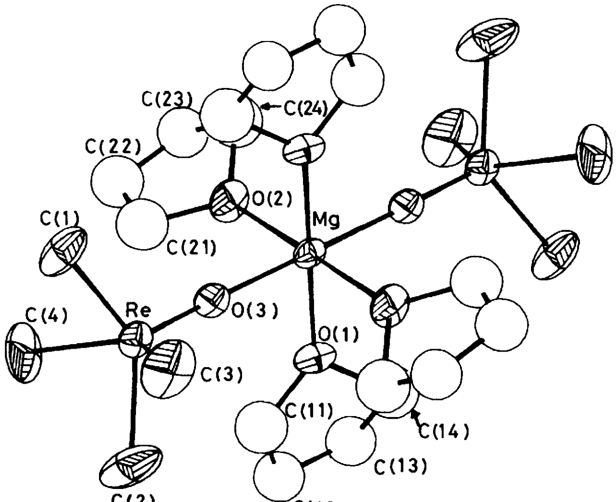

Figure 1. The molecular structure of $(Me_4ReO)_2Mg(thf)_4$

Table 4. Selected bond lengths (Å) and bond angles (°) for $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$

Molecule (I)

O(1A)–Re(1A)	1.742(7)	C(2A)–Si(2A)	1.855(12)	C(1A)–Re(1A)	2.125(12)	C(3A)–Si(3A)	1.847(12)
C(2A)–Re(1A)	2.103(15)	C(4A)–Si(4A)	1.849(14)	C(3A)–Re(1A)	2.134(13)	C(51A)–O(2A)	1.478(13)
C(4A)–Re(1A)	2.107(12)	C(54A)–O(2A)	1.476(15)	O(1A)–Mg(1A)	1.923(7)	C(52A)–C(51A)	1.530(28)
O(2A)–Mg(1A)	2.021(11)	C(53A)–C(52A)	1.389(22)	C(1A)–Si(1A)	1.874(11)	C(54A)–C(53A)	1.533(26)

C(1A)–Re(1A)–O(1A)	109.0(5)	Si(2A)–C(2A)–Re(1A)	120.0(6)	C(4A)–Re(1A)–C(3A)	81.5(5)
C(2A)–Re(1A)–C(1A)	79.9(5)	Si(4A)–C(4A)–Re(1A)	117.4(5)	Mg(1A)–O(1A)–Re(1A)	171.1(4)
C(3A)–Re(1A)–C(1A)	142.7(4)	C(53A)–C(52A)–C(51A)	109.9(16)	C(54A)–O(2A)–Mg(1A)	124.1(8)
C(4A)–Re(1A)–O(1A)	114.2(5)	C(53A)–C(54A)–O(2A)	104.8(11)	Si(1A)–C(1A)–Re(1A)	126.3(7)
C(4A)–Re(1A)–C(2A)	130.2(4)	C(2A)–Re(1A)–O(1A)	115.6(4)	Si(3A)–C(3A)–Re(1A)	136.4(5)
O(2A)–Mg(1A)–O(1A)	100.4(4)	C(3A)–Re(1A)–O(1A)	108.2(4)	C(52A)–C(51A)–O(2A)	100.8(10)
C(51A)–O(2A)–Mg(1A)	128.0(8)	C(3A)–Re(1A)–C(2A)	85.7(6)	C(54A)–C(53A)–C(52A)	106.9(15)
C(54A)–O(2A)–C(51A)	107.9(10)	C(4A)–Re(1A)–C(1A)	81.9(5)		

Molecule (II)

O(1B)–Re(1B)	1.737(10)	C(2B)–Si(2B)	1.846(14)	C(1B)–Re(1B)	2.107(11)	C(3B)–Si(3B)	1.829(12)
C(2B)–Re(1B)	2.145(12)	C(4B)–Si(4B)	1.838(16)	C(3B)–Re(1B)	2.113(12)	C(51B)–O(2B)	1.416(15)
C(4B)–Re(1B)	2.138(14)	C(54B)–O(2B)	1.469(18)	O(1B)–Mg(1B)	1.916(10)	C(52B)–C(51B)	1.480(30)
O(2B)–Mg(1B)	2.015(10)	C(53B)–C(52B)	1.352(25)	C(1B)–Si(1B)	1.858(13)	C(54B)–C(53B)	1.478(25)

C(1B)–Re(1B)–O(1B)	115.0(15)	Si(3B)–C(3B)–Re(1B)	121.3(7)	C(4B)–Re(1B)–C(3B)	82.4(5)
C(2B)–Re(1B)–C(1B)	81.8(5)	C(54B)–O(2B)–C(51B)	107.6(11)	Mg(1B)–O(1B)–Re(1B)	164.2(4)
C(3B)–Re(1B)–C(1B)	128.0(5)	C(53B)–C(52B)–C(51B)	109.1(16)	C(54B)–O(2B)–Mg(1B)	119.1(8)
C(4B)–Re(1B)–O(1B)	107.1(5)	C(53B)–C(54B)–O(2B)	105.1(12)	Si(2B)–C(2B)–Re(1B)	130.0(8)
C(4B)–Re(1B)–C(2B)	145.8(5)	C(2B)–Re(1B)–O(1B)	107.1(5)	Si(4B)–C(4B)–Re(1B)	137.2(6)
O(2B)–Mg(1B)–O(1B)	103.6(4)	C(3B)–Re(1B)–O(1B)	117.1(5)	C(52B)–C(51B)–O(2B)	106.8(13)
C(51B)–O(2B)–Mg(1B)	133.2(9)	C(3B)–Re(1B)–C(2B)	83.7(5)	C(54B)–C(53B)–C(52B)	107.9(13)
Si(1B)–C(1B)–Re(1B)	116.8(7)	C(4B)–Re(1B)–C(1B)	82.4(5)		

are severely disordered (a situation also found in the above tungsten xylidene compound[10]); the O=ReMe$_4$ units also show orientational disorder about the O=Re axis (see Experimental section). The geometry of the rhenium atom is distorted square pyramidal with Re being displaced from the Me$_4$ square by 0.83 Å towards the apical oxo-oxygen. The Re=O and Re–Me bond distances are 1.694(8) and 2.05(6)—2.12(3) Å respectively; the Re–O–Mg bridge is nearly linear [175.0(4)°].

Synthesis and Structure of $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$.—The interaction of Re_2O_7 with the dialkyl or Grignard reagent in thf leads to diamagnetic, air-sensitive red-purple crystals of a complex of the above stoicheiometry that are soluble in and crystallize from hexane. The compound is very soluble in aliphatic or aromatic hydrocarbons and ethers but it reacts with chlorinated solvents. The crystals collapse to a red powder under vacuum, losing thf. The compound has a tendency to co-crystallize with the Grignard reagent and several recrystallizations from hexane are essential to obtain pure material. The same complex may also be obtained in good yields but less cleanly by alkylation of $[Me_3NH][ReO_4]$ with seven, or of $ReOCl_4$ and $ReOCl_3(PPh_3)_2$ with five, equivalents of $Mg(CH_2SiMe_3)Cl$.

The i.r. spectrum of the complex has bands at 1 020s, 970s, 920s, and 880s cm^{-1} that can be assigned to co-ordinated thf or Re=O (probably the band at 970s cm^{-1}) and there are additional bands characteristic for CH_2SiMe_3 groups,[14] Re–C (520 cm^{-1}),[1] and Mg–O (340 cm^{-1}).[12,15]

The ^1H n.m.r. spectrum shows singlets at δ 4.40 and 0.37 p.p.m. (ratio 2:9) that can be assigned respectively to the CH_2 and CH_3 hydrogens of the CH_2SiMe_3 groups. Resonances due to thf were observed at δ 3.44 and 1.24 p.p.m. The $^{13}C-\{^1H\}$ spectrum shows singlets at δ 39.75 and 4.14 p.p.m. which collapse in the 'gated' ^{13}C spectrum to a triplet [J(CH) = 117.58 Hz] and a quartet [J(CH) = 117.82 Hz] respectively; they can be assigned to the methylene and methyl carbons respectively. The thf resonances are at δ 69.59 and 25.22 p.p.m.

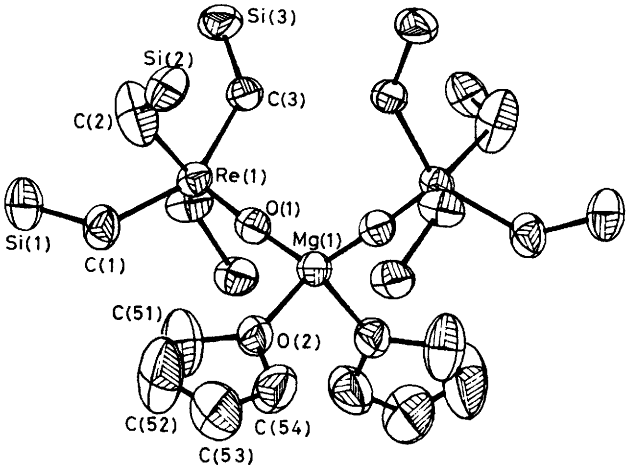

Figure 2. The molecular structure of $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$ (the silyl methyl carbons are omitted for clarity)

Interaction of solutions of the complex with dry oxygen gave a deep blue colour and $ReO(CH_2SiMe_3)_4$ was isolated along with small variable amounts of $Re_2O_3(CH_2SiMe_3)_6$.

The unit cell contains two crystallographically independent molecules both sited on two-fold axes and a diagram of one of these is shown in Figure 2. The geometry of the second molecule is very similar. Selected geometry parameters are given in Table 4. The compound is closely related to the methyl complex but here the magnesium ion carries only two co-ordinated thf molecules and is four-co-ordinate, with a slightly distorted

Table 5. Selected bond lengths (Å) and angles (°) for $Re_2O_3(CH_2SiMe_3)_6$

O(1)–Re	1.671(5)	O(2)–Re	1.856(5)
C(11)–Re	2.114(6)	C(21)–Re	2.132(6)
C(31)–Re	2.133(6)		
O(2)–Re–O(1)	116.1(2)	C(11)–Re–O(1)	106.3(3)
C(21)–Re–O(1)	107.5(3)	C(31)–Re–O(1)	106.8(3)
C(11)–Re–O(2)	137.6(1)	C(21)–Re–O(2)	87.3(2)
C(31)–Re–O(2)	87.4(2)	C(21)–Re–C(11)	80.4(3)
C(31)–Re–C(11)	79.7(3)	C(31)–Re–C(21)	143.9(2)
Si(1)–C(11)–Re	115.9(3)	Si(2)–C(21)–Re	113.0(3)
Si(3)–C(31)–Re	113.6(3)		

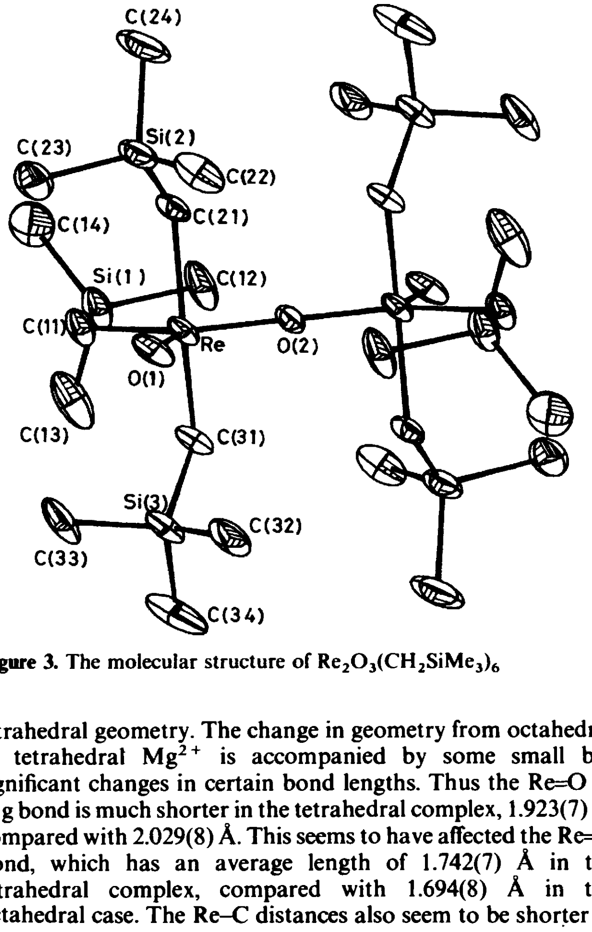

Figure 3. The molecular structure of $Re_2O_3(CH_2SiMe_3)_6$

tetrahedral geometry. The change in geometry from octahedral to tetrahedral Mg^{2+} is accompanied by some small but significant changes in certain bond lengths. Thus the Re=O to Mg bond is much shorter in the tetrahedral complex, 1.923(7) Å, compared with 2.029(8) Å. This seems to have affected the Re=O bond, which has an average length of 1.742(7) Å in the tetrahedral complex, compared with 1.694(8) Å in the octahedral case. The Re–C distances also seem to be shorter in the methyl complex, although this result could be related to the disorder and high thermal motion found in that structure.

Synthesis and Structure of $Re_2O_3(CH_2SiMe_3)_6$.—Alkylation of $ReOCl_3(PPh_3)_3$ by $Mg(CH_2SiMe_3)Cl$[1] gave both the blue paramagnetic $ReO(CH_2SiMe_3)_4$ and the red diamagnetic $Re_2O_3(CH_2SiMe_3)_6$; the latter was formulated with a linear Re–O–Re bridge and *cis*-Re=O groups. It is now clear that this reaction proceeds through the solvated magnesium complex of $[ReO(CH_2SiMe_3)_4]^-$ described above.

The same two compounds can also be obtained by alkylation of $[Me_3NH][ReO_4]$ or Re_2O_7, isolation of $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$, and subsequent oxidation with O_2. However, the overall yields are low and variable, especially for $Re_2O_3(CH_2SiMe_3)_6$. A better procedure is alkylation of the oxo-bridged methoxide,[5] $Re_2O_3(OMe)_6$, which gives high yields.

The previous formulation as a *cis* structure[1] was based only on spectroscopic evidence and a structural determination seemed desirable in view of improved n.m.r. data. The structure as determined is *trans* as shown in Figure 3.

Some important bond lengths and angles are listed in Table 5. The molecule is centrosymmetric with one oxo-oxygen [O(2)] lying on a centre and forming the strictly linear Re–O–Re bridge. The two terminal oxo-groups of the two Re atoms are mutually *trans* but both are *cis* with respect to the bridging oxygen. The geometry around each rhenium is distorted trigonal bipyramidal with O(1), O(2), and C(11) atoms at the equator and C(21) and C(31) on the axis. One of the terminal methyl groups [C(12)] lies very near [*ca.* 0.14 Å] the equatorial plane and makes a close approach of 3.57 Å to Re. This short Re ··· C(12) contact seems to widen significantly the angles O(2)–Re–C(11) [137.6(1)°] and Re–C(11)–Si(1) [115.9(3)°]. The two unique Re–O bonds are significantly different; the bond with the terminal oxygen [1.671(5) Å] is near to the value expected for Re=O whilst the bond length to the bridging oxygen [1.856(5) Å] is consistent with a single Re–O bond shortened due to some Re–O π bonding. Other parameters relating to the molecular geometry are normal.

The spectroscopic data are in accord with the structure. There are singlets in the ^1H n.m.r. spectrum at δ 0.18 and 0.36 p.p.m. (relative intensity 9:18) indicating two types of Me_3SiCH_2 groups. There is also a singlet at δ 3.19 p.p.m. (relative intensity 2) assigned to the CH_2 hydrogens of the equatorial CH_2SiMe_3 groups. The molecule is strictly centrosymmetric and there is a plane of symmetry containing the Re–O–Re axis and the CH_2 groups of the equatorial CH_2SiMe_3 groups which accounts for the equivalence of these CH_2 groups in the ^1H n.m.r. spectrum. However, there is no plane of symmetry containing the Re–O–Re axis and the four axial CH_2 groups and, as a result, these CH_2 groups may be expected to be diastereomeric. The CH_2 hydrogen atoms give rise to two doublets as an AB quartet at δ 3.44 (d, 2 H) and 2.59 (d, 2 H) with J(H–H) = 10.7 Hz (relative intensity 4). The spectrum is thus in agreement with the solid-state structure which persists in solution. The same features are also reflected in the ^{13}C-{^1H} n.m.r. spectrum, which shows two sets of singlets at δ 49.84 and 39.96 p.p.m. that are assigned to the two different types of CH_2 groups, and at δ 2.94 and 2.02 p.p.m. for the CH_3 groups in accordance with assignments made previously[16,17] for CH_2SiMe_3 groups.

The formulation[1] with *cis*-Re=O groups was made in part by comparison with molybdenum(V) complexes containing the $Mo_2O_3^{4+}$ unit,[18] where *cis* and *trans* structures are preferred over the linear O=M–O–M=O unit; two i.r. bands were observed whereas a centrosymmetric *trans* or linear complex should have given one. However, a larger number of complexes with the $Mo_2O_3^{4+}$ unit have only one i.r. band assignable to M=O in the 920—980 cm^{-1} region, irrespective of whether the structure is *cis* or *trans*.[19] For *cis* complexes this is due to either a very small coupling of the two Mo=O oscillators leading to overlap of the two bands, or to a low intensity for the antisymmetric stretch.[20] This could, of course, apply to *cis*-$Re_2O_3^{6+}$ units in rhenium(VI) complexes but no *cis* structures have been established by *X*-ray diffraction. For *trans*-centrosymmetric and linear rhenium(V) structures it would be the case and one band has been observed and assigned to Re=O with the linear $Re_2O_3^{4+}$ unit.[21]

The only Re^{VI} species with a *trans*-$Re_2O_3^{6+}$ unit established by *X*-ray diffraction are $Re_2O_3Cl_6(Re^{VII}O_3Cl)_2$,[22] and the present complexes. The former has only one band at 1 039 cm^{-1} whereas $Re_2O_3(CH_2SiMe_3)_6$ has two, at 1 008 and 990 cm^{-1}, both in solid and solution. Note, however, that $Re_2O_3Me_6$ (see below) which is *trans* (although not a strictly centrosymmetric molecule), has only one band. It seems most reasonable, in view of the known structure that one of the two bands in $Re_2O_3(CH_2SiMe_3)_6$ should either be assigned to a vibration of

Table 6. Selected bond lengths (Å) and bond angles (°) for $Re_2O_3Me_6$

O(1)–Re(1)	1.833(3)	O(2)–Re(1)	1.743(20)
O(2A)–Re(1)	1.742(18)	C(1)–Re(1)	2.195(28)
C(1A)–Re(1)	2.200(36)	C(2)–Re(1)	2.169(25)
C(2A)–Re(1)	2.345(32)	C(3)–Re(1)	2.122(24)
C(3A)–Re(1)	2.288(22)		
O(2)–Re(1)–O(1)	110.8(8)	O(2A)–Re(1)–O(1)	112.2(9)
C(1)–Re(1)–O(1)	138.7(5)	C(1)–Re(1)–O(2)	109.2(10)
C(1)–Re(1)–O(2A)	106.0(10)		
C(1A)–Re(1)–O(1)	154.4(7)	C(1A)–Re(1)–O(2)	94.7(11)
C(1A)–Re(1)–O(2A)	87.0(11)		
C(2)–Re(1)–O(1)	88.7.8)	C(2)–Re(1)–O(2)	117.7(9)
C(2)–Re(1)–O(2A)	81.9(10)	C(2)–Re(1)–C(1)	81.5(10)
C(2)–Re(1)–C(1A)	77.0(11)		
C(2A)–Re(1)–O(1)	78.2(8)	C(2A)–Re(1)–O(2)	140.6(7)
C(2A)–Re(1)–O(2A)	104.8(10)	C(2A)–Re(1)–O(1)	77.4(11)
C(2A)–Re(1)–C(1A)	80.6(12)		
C(3)–Re(1)–O(1)	90.2(8)	C(3)–Re(1)–O(2)	88.4(10)
C(3)–Re(1)–O(2A)	123.7(11)	C(3)–Re(1)–C(1)	81.1(11)
C(3)–Re(1)–C(1A)	92.8(11)	C(3)–Re(1)–C(2)	152.3(9)
C(3)–Re(1)–C(2A)	130.7(8)		
C(3A)–Re(1)–O(1)	82.3(8)	C(3A)–Re(1)–O(2)	108.2(10)
C(3A)–Re(1)–O(2A)	143.5(10)	C(3A)–Re(1)–C(1)	76.0(11)
C(3A)–Re(1)–C(1A)	92.1(11)	C(3A)–Re(1)–C(2)	133.4(9)
C(3A)–Re(1)–C(2A)	111.1(10)		

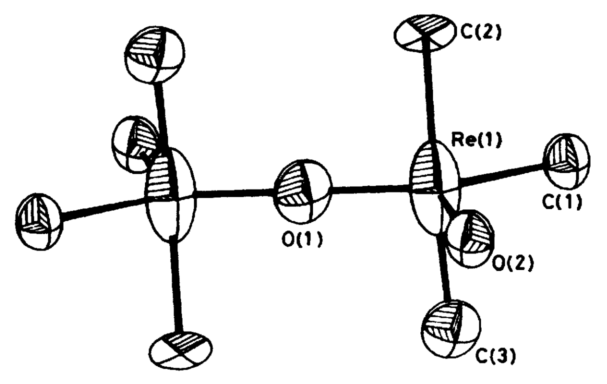

Figure 4. The molecular structure of $Re_2O_3Me_6$ (only the disorder component with the major occupancy is shown)

the CH_2SiMe_3 group (indeed such bands in the range 1 000—800 cm^{-1} have been established in numerous trimethylsilylmethyl compounds as fundamentals involving the various $-CH_2-$ angular movements, predominantly wagging and twisting[14]), or less likely attributed to an undetected rhenium oxo-species formed by slight decomposition of the original material. Note that one band is observed only when using freshly recrystallized $Re_2O_3Me_6$ (see below); material aged for several days even under nitrogen or argon shows splitting of the original peak as in the trimethylsilylmethyl complex.

Synthesis and Structure of $Re_2O_3Me_6$.—This compound is readily obtained in high yield by interaction of $Me_3SiOReO_3$ with three equivalents of trimethylaluminium in hexane, as diamagnetic, air-sensitive fine red needles from hexane. The compound sublimes at *ca.* 50 °C (10^{-1} mmHg) and is very soluble in aromatic, aliphatic, and halogenated hydrocarbons, ethers, acetonitrile, and acetone, but is insoluble in and unaffected by water. Attempts to determine the structure of this complex by *X*-ray methods were fraught with difficulties due to almost universal twinning of the crystals, irrespective of the method of crystallisation. However, one specimen was eventually obtained that was almost single, albeit of poor quality (see Experimental section) and an approximate structure was eventually obtained. This showed the molecule to have a *trans* structure analogous to that found for the CH_2SiMe_3 complex. A diagram of the molecule is given in Figure 4 and selected bond lengths and angles in Table 6. In view of the low accuracy of the structural parameters, it is not possible to make any detailed comparison of the geometries of the methyl and trimethylsilylmethyl analogues.

The spectroscopic data are in good agreement with the structure. The i.r. spectrum has a strong band at 1 020 cm^{-1} (Re=O), a broad band at 850 cm^{-1} [$\nu_{asym.}$(Re–O–Re)] and a weak band at 550 cm^{-1} (Re–C). No other bands occur in the region 400—550 cm^{-1} that are characteristic of a bent μ-oxo-structure $\mathrm{Re}{\diagup}^{\mathrm{O}}{\diagdown}\mathrm{Re}$.[5,23,24] The shift of the asymmetric ReORe mode from the normal range (660—720 cm^{-1}) for linear OReOReO units up to the 750—860 cm^{-1} region for *cis/trans* isomers and linear ReORe units without terminal oxygens is the most characteristic sign of a *cis*- or *trans*-Re_2O_3 unit with linear Re–O–Re groups.[1,20–25]

The ^1H n.m.r. spectrum has singlets at δ 2.31 and 2.19 p.p.m. (ratio 1:2) indicating two types of methyl groups while the $^{13}C-\{^1H\}$ spectrum also has two singlets at δ 39.92 and 30.08 p.p.m. which collapse to quartets in the 'gated' ^{13}C spectrum, *J*(C–H) = 129.27 and 131.79 Hz respectively. The non-equivalence of the methyl groups is analogous to that observed for the trimethylsilylmethyl groups in $Re_2O_3(CH_2SiMe_3)_6$ and is consistent with a non-linear OReOReO unit [note the equivalence of the neopentyl groups in $W_2O_3(CH_2CMe_3)_6$ with a linear OWOWO structure[26]].

It appears that *cis*- and *trans*-M_2O_3 isomers are more favoured for the coupling of the single electron through the oxygen bridge in d^1 systems (Mo^V, Re^{VI}) than linear OMOMO units.[18,19,27] The latter is observed without exception in a great number of Re^V (d^2) compounds and more recently in the W^{VI} (d^0) complex $W_2O_3(CH_2CMe_3)_6$, the structure of which contrasts sharply with the structure of $Re_2O_3(CH_2SiMe_3)_6$. Note also the contrast between the structures of the dithiocarbamates $Re^V{}_2O_3(S_2CNEt_2)_4$[27] and $Mo^V{}_2O_3(S_2CNPr^i{}_2)_4$[28] which have respectively linear and *cis*-M_2O_3 units.

The o-*Xylenediyl Derivative*, $\{[o\text{-}(CH_2)_2C_6H_4]_2ReO\}_2Mg(thf)_4$.—Attempts to prepare the rhenium analogue of the oxotungsten *o*-xylidene magnesium complex[10] by treating either $[Me_3NH][ReO_4]$ or Re_2O_7 with the di-Grignard reagent *o*-$C_6H_4(CH_2MgCl)_2$[29] were unsuccessful; oily materials were obtained from an otherwise clean reaction. However, the compound can be isolated in good yield by treating $[ReO_2(PMe_3)_4][BPh_4]$[30] with 3.5 equivalents of *o*-$C_6H_4(CH_2MgCl)_2$ in thf solutions. The compound crystallizes from a toluene–thf mixture as bright orange-red, air-sensitive needles readily soluble in ethers and mixtures of thf and aromatic hydrocarbons but insoluble in hexane. As for the methyl and trimethylsilylmethyl rhenium analogues and the *o*-xylidene tungsten complex, the compound loses thf on heating above 130 °C or under vacuum and collapses to a red powder.

We have been unable so far to obtain crystals suitable for *X*-ray analysis due to twinning. The i.r. spectrum shows peaks at 1 032, 1 023, and 1 010 cm^{-1} attributed to ν(C–O–C) and a sharp band at 936 cm^{-1} due to ν(Re=O); by comparison with the tungsten analogue the peak at 450 cm^{-1} is attributed to ν(Re–C) and the bands at 370 and 320 cm^{-1} to ν(Mg–O).[12]

The ^{1}H n.m.r. spectrum shows a sharp singlet at δ 2.10 p.p.m. assigned to the methylene protons and bands at δ 3.56 and 1.40 p.p.m. due to co-ordinated thf. The protons at the aromatic ring appear as multiplets at δ 7.03 and 6.92 p.p.m. The ^{13}C-{^{1}H} spectrum shows bands at δ 70.81 and 25.22 p.p.m. for co-ordinated thf while the methylene carbon appears as a sharp peak at δ 36.15 p.p.m. Peaks at δ 137.28, 128.79, and 125.45 p.p.m. are assigned to the aromatic carbons.

Experimental

Microanalyses were by Pascher, Bonn. Spectrometers were as follows: i.r., Perkin-Elmer 683 (spectra of Nujol mulls, values in cm^{-1}); n.m.r., Bruker WM-250 and JEOL FX 900 (data given in p.p.m. relative to $SiMe_4$); mass, VG Micromass 7070 and MS-9.

Trimethylammonium per-rhenate was prepared by dissolving rhenium in 30% H_2O_2 and neutralising the solution with NMe_3; the salt was crystallised from water. Re_2O_7, $Me_3SiOReO_3$,[31] and $[ReO_2(PMe_3)_4][BPh_4]$[30] were prepared as before. The petroleum used had b.p. 40—60 °C. Solvents were refluxed over sodium or sodium–benzophenone under nitrogen and distilled before use. All operations were carried out under vacuum or purified argon.

1. *Tetrakis(tetrahydrofuran)magnesium Bis[tetramethyloxorhenate*(V)].—To a suspension of $[Me_3NH][ReO_4]$ (1.0 g, 3.22 mmol) in thf (30 cm^3) at −78 °C was added MgMeCl (23.5 cm^3 of a 0.96 mol dm^{-3} solution in Et_2O, 22.56 mmol). The mixture was allowed to warm to room temperature with stirring. The orange-red solution was evaporated and the residue extracted with toluene (2 × 20 cm^3); the filtered extract was reduced to 25 cm^3 and cooled to −20 °C to give red-brown polyhedra. It was recrystallised from toluene–thf. Yield: 0.24 g, 17.8%. I.r.: ν(Re=O) 960s br; other 1 260w, 1 210w, 1 035s br, 920 (sh), 890m br, 680w, 540m br, 370m br, 320m br.

2. *Bis(tetrahydrofuran)magnesium Bis[oxotetrakis(trimethylsilylmethyl)rhenate*(V)].—To a stirred suspension of Re_2O_7 (0.93 g, 1.92 mmol) in thf (30 cm^3) at −78 °C was added $Mg(CH_2SiMe_3)Cl$ (29.9 cm^3 of a 0.9 mol dm^{-3} solution in Et_2O, 26.91 mmol) and the solution was allowed to warm up and kept at room temperature for *ca.* 0.5 h. Evaporation of the red solution and extraction of the residue with light petroleum (2 × 20 cm^3) followed by filtration of the extracts and reduction of these to *ca.* 15 cm^3 led to red-purple crystals on cooling at −78 °C. These were recrystallised from hexane several times until well shaped crystals were obtained. Yield: 0.67 g, 21.5%. I.r.: ν(Re=O) 970s; other 1 400w, 1 295w, 1 250s, 1 240s, 1 020s, 940s, 920s, 880s, 830s br, 750m, 680s, 610w, 520w, 480m br, 340m br.

3. μ-*Oxo-bis[oxotris(trimethylsilylmethyl)rhenium*(VI)].—*Method* A. To a cooled (−78 °C) solution of $Re_2O_3(OMe)_6$[5] (0.3 g, 0.49 mmol) in Et_2O (20 cm^3) was added $Li(CH_2SiMe_3)$ (3.1 cm^3 of a 0.95 mol dm^{-3} solution in Et_2O, 2.94 mmol). The solution was warmed slowly to room temperature, the thf removed and the residue extracted into hexane (2 × 20 cm^3), concentration of which (to *ca.* 5 cm^3) and cooling (−20 °C) gave the complex. Yield: 0.42 g, 90%.

Method B. To a stirred suspension of Re_2O_7 (1.61 g, 3.32 mmol) in thf (30 cm^3) at −78 °C was added $Mg(CH_2SiMe_3)Cl$ (25.8 cm^3 of a 0.9 mol dm^{-3} solution in Et_2O, 23.22 mmol). The solution, which becomes red-purple, was allowed to warm to room temperature. The solvent was removed under vacuum and the residue extracted with light petroleum (2 × 20 cm^3). Dry oxygen was bubbled through the solution at −78 °C until the colour became blue. The product was isolated by chromatography as before[1] giving a blue band of $ReO(CH_2SiMe_3)_4$ and a smaller red band which was collected, concentrated to *ca.* 5 cm^3, and cooled to −20 °C to yield red needles. Yield: 0.2 g, 9%. I.r.: ν(Re=O) 990s (1 008s); other 1 410w, 940m, 830br, 800s, 680s, 610w, 550w, 525w.

Table 7. Crystallographic data

Compound	$(Me_4ReO)_2Mg(thf)_4$	$[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$	$Re_2O_3(CH_2SiMe_3)_6$	$Re_2O_3Me_6$
M	837.42	1 270.662	943.70	510.608
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
a/Å	10.437(3)	24.830(2)	12.034(3)	5.119(1)
b/Å	9.951(3)	11.574(2)	12.005(2)	7.019(4)
c/Å	9.510(3)	24.262(3)	8.725(1)	9.468(4)
α/°	78.95(3)	90.00	110.24(1)	79.46(4)
β/°	63.50(2)	113.59(2)	105.89(1)	76.30(2)
γ/°	69.50(2)	90.00	64.17(2)	68.15(5)
U/Å^3	827.2	6 389.80	1 053.1	306.15
Space group	$P\bar{1}$	$P2/c$	$P\bar{1}$	$P\bar{1}$
Z	1	4	1	1
F(000)	410	2 592	468	282
D_c/ g cm^{-3}	1.68	1.32	1.49	2.76
Crystal size/mm	0.35 × 0.25 × 0.15	0.3 × 0.45 × 0.2	0.46 × 0.18 × 0.10	0.125 × 0.30 × 0.50
μ(Mo-K_α)/cm^{-1}	74.3	39.95	59.8	199.9
Transmission range	0.635—0.999	0.813—0.999	0.842—0.998	0.195—0.998
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 25	1.5, 25	1.5,25	1.5, 25
Total no. of reflections collected	2 993	9 285	3 772	1 117
Total unique	2 915	8 869	3 710	1 072
Total observed	2 490	5 182	3 299	796
n in $[F_o > n\sigma(F_o)]$	3	4	3	4
No. of parameters	159	602	188	88
Weighting scheme parameter g in $w = 1/[\sigma^2(F_o) + gF_o^2]$	0.0008	0.0001	0.0002	0.000 01
Final R $[\Sigma\Delta F/\Sigma F_o]$	0.0512	0.0372	0.0230	0.0727
Final $R'\{[\Sigma w\Delta F^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$	0.0645	0.0344	0.0270	0.0668

4. *μ-Oxo-bis[trimethyloxorhenium*(VI)].—To a hexane (20 cm^3) solution of Me$_3$SiOReO$_3$ (0.5 g, 1.5 mmol) was added a solution of Al$_2$Me$_6$ (4.5 mmol, 2 mol dm^{-3} in hexane). The resulting deep orange solution was allowed to warm to room temperature, then recooled (-20 °C) and degassed water (5 cm^3) added. The mixture was warmed until the ice melted then immediately cooled to -20 °C and the mixture filtered. The orange-red solution was concentrated (*ca.* 3 cm^3) and cooled (-78 °C) to give orange-red needles which were collected and dried under vacuum. Yield: 0.31 g, 78%. The yield of crude product if the water-washed and dried hexane solution is evaporated is virtually quantitative and subsequent losses on crystallisation are due to the high solubility in hexane.

Table 8. Fractional co-ordinates ($\times 10^4$) and occupation factors for (Me$_4$ReO)$_2$Mg(thf)$_4$

Atom	*x*	*y*	*z*	*k**
Re	1 813.9(4)	2 589.9(4)	2 895.7(4)	1.0
Mg	5 000*	0*	0*	1.0
O(1)	5 086(9)	−1 566(8)	1 810(8)	1.0
O(2)	3 538(9)	−776(9)	−302(9)	1.0
O(3)	3 214(7)	1 357(7)	1 605(7)	1.0
C(1)	493(36)	4 163(32)	1 907(33)	0.65
C(1A)	−197(49)	3 465(61)	2 574(82)	0.35
C(2)	1 717(61)	1 957(47)	5 179(39)	0.65
C(2A)	2 341(77)	3 070(170)	4 540(110)	0.35
C(3)	2 407(43)	4 323(39)	3 162(48)	0.65
C(3A)	2 095(111)	4 595(47)	2 235(71)	0.35
C(4)	−245(31)	2 117(45)	4 011(51)	0.65
C(4A)	327(67)	1 737(61)	4 896(80)	0.35
C(11)	4 102(26)	−1 532(26)	3 459(27)	0.90
C(12)	4 426(25)	−2 998(24)	4 192(26)	0.90
C(13)	5 736(23)	−3 888(23)	3 001(23)	0.90
C(14)	6 485(31)	−2 830(30)	1 806(31)	0.80
C(15)	5 500(43)	−3 134(42)	1 640(45)	0.50
C(21)	1 950(34)	−644(33)	803(35)	0.70
C(22)	1 496(36)	−1 680(34)	237(38)	0.70
C(23)	2 701(34)	−2 259(33)	−1 154(35)	0.70
C(24)	1 988(52)	−1 261(52)	−1 361(53)	0.60
C(25)	3 760(63)	−2 326(70)	−549(73)	0.60
C(26)	3 671(37)	−1 262(37)	−1 774(40)	0.70

* Invariant parameter.

The mass spectrum shows the molecular ion at either 70 eV [512 (20.6%) Re^{187}Re^{187}, 510 (27.8) Re^{185}Re^{187}, 508 (10.3) Re^{185}Re^{185}] or at 12 eV [512 (13.2%), 510 (16.0%), 508 (4.5%)]. The peak intensities are in good agreement with those calculated for the rhenium isotopic distribution (^{185}Re 37.40, ^{187}Re 62.60%). The base peak in both spectra occurs at *m/e* 248, corresponding to ReOMe$_3{}^+$. I.r.: ν(Re=O) 1 020s; other 1 260w, 1 225m, 1 190w, 850m br, 550w.

5. *Tetrakis(tetrahydrofuran)magnesium Bis[oxobis(*o*-xylenediyl)rhenate*(V)].—To a suspension of [ReO$_2$(PMe$_3$)$_4$][BPh$_4$] (1.2 g, 1.43 mmol) in thf (30 cm^3) at -78 °C was added *o*-C$_6$H$_4$(CH$_2$MgCl)$_2$ (66.73 cm^3 of a 0.075 mol dm^{-3} solution in thf, 5.05 mmol). The solution was warmed slowly to room temperature over *ca.* 1 h, the solvent was removed under vacuum and the residue extracted with toluene (2 × 30 cm^3). Concentration to *ca.* 20 cm^3, followed by cooling to -20 °C, gave orange-red needles which can be recrystallized from a thf–toluene mixture (1:1). Yield 0.18 g, 22%. I.r.: ν(Re=O) 936s; other 1 290m, 1 260w, 1 210w, 1 160w, 1 140w, 1 032s, 1 023 (sh), 1 010s, 925 (sh), 915s, 880m, 740s, 730 (sh), 450m, 370m, 320m.

X-Ray Crystallography.—Crystals of the compounds were mounted under argon in Lindemann capillaries. Unit-cell parameters were obtained by least-squares refinement of the setting angles for 25 reflections measured on a CAD4 diffractometer. Intensities were recorded in the ω–2θ scan mode

Table 9. Fractional atomic co-ordinates ($\times 10^4$) for [(Me$_3$SiCH$_2$)$_4$ReO]$_2$Mg(thf)$_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1A)	3 854(0.5)	5 198(0.5)	1 263(0.5)	Re(1B)	1 172(0.5)	1 157(0.5)	2 279(0.5)
Mg(1A)	5 000*	3 681(4)	2 500*	Mg(1B)	0*	−360(4)	2 500*
Si(1A)	2 325(1)	4 712(4)	403(2)	Si(1B)	2 202(1)	−248(3)	3 448(1)
Si(2A)	3 708(2)	6 757(3)	2 398(1)	Si(2B)	1 869(2)	3 951(3)	2 711(2)
Si(3A)	3 987(2)	7 925(3)	534(2)	Si(3B)	47(2)	2 554(4)	1 146(2)
Si(4A)	4 130(2)	3 522(3)	264(1)	Si(4B)	1 720(2)	113(4)	1 155(2)
O(1A)	4 407(3)	4 402(5)	1 809(3)	O(1B)	666(3)	471(6)	2 495(3)
O(2A)	4 511(3)	2 478(6)	2 693(3)	O(2B)	−157(3)	−1 550(6)	1 848(3)
C(1A)	3 041(4)	4 315(10)	1 026(4)	C(1B)	2 058(4)	759(9)	2 808(4)
C(2A)	3 405(5)	6 375(11)	1 588(4)	C(2B)	1 413(5)	2 743(9)	2 776(4)
C(3A)	4 243(4)	6 686(8)	1 054(5)	C(3B)	835(4)	2 267(10)	1 525(4)
C(4A)	3 715(5)	4 764(9)	373(4)	C(4B)	1 321(5)	48(10)	1 649(5)
C(11A)	2 124(6)	3 613(13)	−216(6)	C(11B)	1 876(5)	−1 707(10)	3 198(5)
C(12A)	2 310(5)	6 182(11)	57(5)	C(12B)	3 015(5)	−454(11)	3 817(5)
C(13A)	1 724(6)	4 719(17)	678(7)	C(13B)	1 940(6)	323(11)	4 008(5)
C(21A)	4 200(10)	8 012(19)	2 574(9)	C(21B)	2 346(7)	3 589(13)	2 306(8)
C(22A)	4 120(8)	5 603(13)	2 919(6)	C(22B)	1 431(7)	5 191(12)	2 268(9)
C(23A)	3 090(7)	7 202(19)	2 583(7)	C(23B)	2 352(10)	4 481(20)	3 455(7)
C(31A)	3 653(7)	7 514(12)	−291(6)	C(31B)	−78(7)	3 448(16)	481(6)
C(32A)	4 649(6)	8 812(12)	625(7)	C(32B)	−243(9)	3 301(23)	1 625(9)
C(33A)	3 440(7)	8 873(12)	643(7)	C(33B)	−375(10)	1 250(20)	931(13)
C(41A)	3 936(6)	3 399(13)	−569(5)	C(41B)	1 777(7)	−1 377(14)	897(7)
C(42A)	4 939(5)	3 745(12)	653(6)	C(42B)	2 470(7)	659(20)	1 493(9)
C(43A)	3 900(5)	2 143(10)	526(6)	C(43B)	1 334(8)	932(18)	449(6)
C(51A)	3 866(5)	2 344(12)	2 423(6)	C(51B)	−646(6)	−1 776(15)	1 303(6)
C(52A)	3 763(6)	1 786(17)	2 945(8)	C(52B)	−453(8)	−2 648(20)	973(8)
C(53A)	4 254(7)	1 151(13)	3 300(7)	C(53B)	132(8)	−2 814(16)	1 264(7)
C(54A)	4 760(6)	1 534(11)	3 131(6)	C(54B)	317(6)	−2 341(13)	1 879(7)

* Invariant parameter.

Table 10. Fractional co-ordinates (× 10^4) for the non-hydrogen atoms in $Re_2O_3(CH_2SiMe_3)_6$

Atom	*x*	*y*	*z*
Re	3 296.6(2)	453.4(2)	4 847.9(2)
Si(1)	1 966(1)	792(2)	985(2)
Si(2)	2 452(2)	3 583(1)	6 820(2)
Si(3)	3 118(2)	−2 405(1)	4 135(3)
O(1)	2 804(4)	572(3)	6 533(4)
O(2)	5 000*	0*	5 000*
C(11)	1 693(4)	875(5)	3 056(6)
C(12)	3 607(5)	506(8)	922(7)
C(13)	1 628(7)	−575(8)	−647(8)
C(14)	905(7)	2 310(8)	422(10)
C(21)	3 609(4)	2 330(4)	4 905(6)
C(22)	3 416(7)	3 192(6)	8 789(7)
C(23)	796(6)	3 812(7)	6 755(11)
C(24)	2 484(8)	5 104(6)	6 724(13)
C(31)	3 546(5)	−1 426(4)	3 283(6)
C(32)	4 111(6)	−2 681(6)	6 099(8)
C(33)	1 447(6)	−1 657(7)	4 404(9)
C(34)	3 362(10)	−3 976(7)	2 537(12)

* Invariant parameter.

Table 11. Fractional atomic co-ordinates (× 10^4) and occupation factors for $Re_2O_3Me_6$

Atom	*x*	*y*	*z*	*k**
Re(1)	3 285(2)	4 055(2)	1 778(1)	1.0
O(1)	5 000*	5 000*	0*	0.50
O(2)	317(32)	3 512(29)	1 608(24)	0.60
O(2A)	−423(35)	4 993(33)	1 997(28)	0.40
C(1)	4 253(36)	2 861(34)	3 973(29)	0.60
C(1A)	2 706(41)	3 290(40)	4 166(38)	0.40
C(2)	2 544(37)	6 955(33)	2 567(30)	0.60
C(2A)	4 476(40)	6 677(39)	2 405(36)	0.40
C(3)	5 814(38)	983(36)	1 382(32)	0.60
C(3A)	7 208(40)	1 168(39)	1 405(37)	0.40

* Invariant parameter.

with Mo-K_α radiation (λ = 0.710 69 Å) by following standard procedures.[32] Semi-empirical absorption corrections were applied to data sets using the ω-scan values for three reflections in each case. Further experimental data are given in Table 7.

The structures were solved using Patterson and difference electron-density syntheses and refined by full-matrix least-squares using SHELX-76.[33] For the final refinements, a weighting scheme of the type $w = 1/[\sigma^2(F_o) + gF_o^2]$ was used, with values of *g* chosen to give acceptable agreement analyses. For $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$ and $Re_2O_3(CH_2SiMe_3)_6$, the heavy atoms (Re, Mg, C, O, Si) were refined with anisotropic thermal parameters; hydrogens were inserted in calculated positions and refined as part of rigid groups (CH_3 or CH_2), with group isotropic thermal parameters. Solution and refinement of $(Me_4ReO)_2Mg(thf)_4$ was made difficult by both poor quality data and disorder in parts of the structure. The Re, Mg, and all the O atoms, none of which was disordered, refined with reasonable anisotropic thermal parameters. The four methyl groups on each Re are disordered in such a way that one set of four positions has occupancy of 0.65 while the other set 0.35, the two sets being coplanar within experimental error and mutually rotated about the Re–O axis by *ca.* 35°. The four methyl carbons were finally refined anisotropically in eight positions with fixed occupancies. In contrast, the disordering of the carbons of the two independent thf groups is more complicated; a total of five and six positions for the two thf groups, as indicated by the significant peaks in the difference maps, were refined with fractional occupancies fixed but one U_{iso} was allowed to vary for each position. The final difference map still contained several ripples (*ca.* 1 e Å^{-3}) around these carbons suggesting that the disordered models for the thf groups are not totally adequate.

Refinements of the structure of $Re_2O_3Me_6$ caused even greater proplems. As mentioned previously (see Discussion section) crystals of this compound tend to occur as twins. The specimen finally used for the analysis, whilst being essentially single, gave reflections of widely varying widths, a feature also demonstrated on Weissenberg photographs. Probably as a result of this, the positions of the terminal oxo-oxygen and methyl carbons showed large apparent anisotropy of the thermal motion and/or split peaks and it proved difficult to obtain stable refinement. Attempts were made to refine in space group *P*1, but these were quite unsuccessful. Eventually, the refinement process was terminated with the atoms all assigned anisotropic thermal parameters but with the oxo-oxygen and methyl carbons each adopting two nearby sites, with linked occupancies totalling unity.

The final atomic parameters are given in Tables 8—11. Sources of scattering factor data were as in ref. 5. All calculations were made on a DEC VAX11/750 computer.

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